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Gaseous, Particulate, and Sulfur-Related Emissions from Non-Catalyst and Catalyst Equipped Vehicles

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GASEOUS, PARTICULATE, AND SULFUR-RELATED EMISSIONS FROM NON-CATALYST AND CATALYST EQUIPPED VEHICLES

by

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ABSTRACT

The gaseous, particulate, and sulfur-related emissions from six 49-state 1975 domestic production catalyst equipped vehicles (two Chevrolets, two Fords, and two Plymouths) and one 1975 imported prototype non-catalyst vehicle (Honda CVCC) were measured by a variety of chemical analysis techniques as a function of fuel sulfur level. Four separate and different sulfur level fuels were tested for each vehicle. The seven test vehicles were driven alternatingly, in accordance with the 1975 Federal Test Procedure (75 FTP) and Highway Fuel Economy Test (HWFET) procedures. All vehicles tested met the level of the 1975 interim emission standards of 1.5 g/mile hydrocarbon (HC), 15 g/mile carbon monoxide (CO), and 3.1 g/mile oxides of nitrogen (NO_x). The Honda CVCC gave the lowest gaseous emissions and best fuel economy. Retarding the stock spark timing 5° on those vehicles that "pinged" on the regular no lead test fuel eliminated the pinging, but decreased fuel economy and increased regulated emissions. Sulfur dioxide (SO_2), particulate matter, and sulfate emissions increased with increasing fuel sulfur and were greater during the HWFET cycle than during the 75 FTP cycle. The greatest particulate and sulfate emitters were the air pump equipped Ford vehicles, while the lowest particulate and sulfate emitter was the Honda CVCC. Particulate matter was composed mostly of sulfuric acid; the non-sulfate portion of the particulate matter was composed of carbonaceous material and aluminum and iron oxidation products. No platinum was found in the particulate matter.

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SECTION 1

INTRODUCTION

It has been demonstrated that oxidation catalyst equipped vehicles emit more particulate matter, consisting mostly of aqueous sulfuric acid (H_2SO_4) droplets, than do their non-catalyst equipped counterparts.[1] Because concern has been expressed about the environmental impact of these sulfate emissions[2,3] we have undertaken a study of six 49-state 1975 production catalyst cars and one 1975 prototype non-catalyst vehicle. This study examines the gaseous and particulate emissions of these vehicles as a function of fuel sulfur, type of catalyst, and driving cycle with particular emphasis upon sulfate formation.

BACKGROUND

With the advent of the 1975 automobiles, we were introduced to a new auto exhaust emission control device -- the catalytic converter.[4] This device, which oxidizes excess hydrocarbons (HC) and carbon monoxide (CO) in the exhaust, replaces former fuel inefficient controls such as retarded spark timing. Consequently, auto manufacturers in 1975 were able to increase fuel economy substantially, 10-20% over 1974 model automobiles, while meeting the tighter 1975-1977 interim exhaust emission standards. In addition to an increase in fuel economy, there was also an improvement in the driveability of 1975 automobiles compared to previous years. Although the catalytic converter emission control device decreases regulated gaseous emissions, it unfortunately increases non-regulated particulate emissions under certain operating conditions, specifically that of sulfuric acid (H_2SO_4). This emission of sulfuric acid is a product of the combustion of fuel sulfur and the mechanism of catalytic oxidation. In the following pages we shall look in some detail at

how the catalytic converter functions.

Most catalysts, including those studied in this work, are composed of noble metal Pt/Pd (platinum/palladium) blend. The Pt/Pd blend was chosen because of its relative chemical inertness and its resistance to chemical poisoning, especially by sulfur compounds. Approximately 1.5 grams of the noble metal blend are used per catalyst. Currently there are two geometric catalyst configurations: pellet (beaded) and monolith. The container shape of the pelleted catalyst is a bedpan and, internally, the pelleted catalysts contain pellets approximately 1/6 - 3/8 inch in diameter composed mostly of alumina. The pelleted catalysts used in this study had an internal volume of 260 cubic inches and exhibited a large surface area per unit mass. The container shape of the monolithic catalyst is an elliptical cylinder approximately 3-6 inches in diameter. Internally, the monoliths contain a honeycomb type structure extending the length and diameter of the cylinder and are surrounded by an integral outer skin of alumina or corderite. Compared to pellet catalysts, monoliths offer greater mechanical strength, lower pressure drop, smaller surface area per unit mass, and quicker warm-up time. Both types of catalysts are mounted before the automobile muffler, as close as possible to the engine's exhaust manifold on the exhaust pipe.

SECTION 2

CONCLUSIONS

On basis of the gaseous, particulate, and sulfur-related emission results obtained from the seven vehicles in the experimental test program, the following conclusions apply:

1. All test vehicles met the level of the 1975 interim gaseous emission standard of 1.5 g/mile HC, 15 g/mile CO, and 3.1 g/mile NO_x.

2. Retarding the stock spark timing 5° from manufacturer specifications on those vehicles that "pinged" on the unleaded test fuel eliminated the "pinging" at the expense of decreased fuel economy and increased regulated gaseous emissions.

3. Sulfur dioxide, particulate matter, and sulfate emission rates increased with increasing fuel sulfur.

4. Total sulfur balances were related to driving cycle characteristics. 1975 FTP sulfur balances were consistently less than HWFET sulfur balances.

5. The sulfur oxide storage/release phenomenon depended upon the type and operating conditions of the catalyst. Pelleted catalysts were among the lowest 1975 FTP sulfate emitters and among the highest HWFET emitters. The air pump equipped monolithic catalysts emitted the greatest sulfate and particulate matter in both the 1975 FTP and HWFET.

6. The catalyst vehicles' particulate matter was composed mostly of sulfate material and its associated bound water molecules. The non-sulfate portion of the particulate was composed of carbonaceous material and inorganic oxidation products. Iron and aluminum were the most prominent inorganic oxidation products emitted. No platinum was detected in the particulate matter.

7. The non-catalyst vehicle's particulate matter was composed mostly of carbonaceous material.

SECTION 3

MECHANISM OF SULFATE FORMATION

In the combustion process detailed in Figure 1, the fuel sulfur is oxidized to sulfur dioxide (SO_2). The exhaust gases, including hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_x), and sulfur dioxide (SO_2) then proceed via the exhaust manifold to the oxidation catalyst. In the catalyst, excess hydrocarbons and carbon monoxide are oxidized to water vapor [$H_2O(g)$] and carbon dioxide (CO_2), while some of the SO_2 is oxidized to sulfur trioxide (SO_3). Proceeding through the catalyst and into the muffler, the SO_3 combines with H_2O (g) to form gaseous H_2SO_4. This gaseous H_2SO_4 condenses to a finely dispersed aerosol after exiting from the tailpipe.

In dealing with formation of sulfuric acid in the exhaust, one must consider the following reactions:

(1) $S + O_2 \longrightarrow SO_2$ (g)	Assume complete combustion of fuel sulfur to SO_2
(2) $SO_2 + 1/2\ O_2 \longrightarrow SO_3$ (g)	Oxidation of SO_2 to SO_3 via catalyst
(3) $SO_3 + H_2O \longrightarrow H_2SO_4$ (g)	Hydration of SO_3 to gaseous H_2SO_4
(4) $H_2SO_4(g) + n\ H_2O \longrightarrow$ $H_2SO_4 \cdot nH_2O$	Condensation of gaseous H_2SO_4 to finely dispersed aerosol outside tailpipe

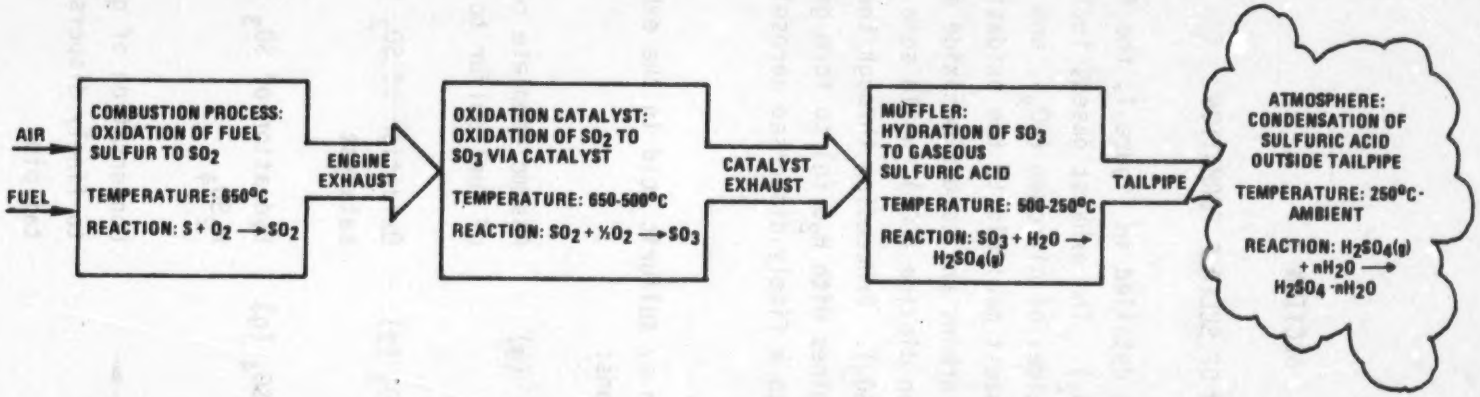

Figure 1. Schematic of sulfur oxidation reactions throughout the exhaust system.

It is apparent that the sulfate determining reaction is reaction (2), which is the heterogeneous catalytic oxidation of SO_2 to SO_3.

A probable mechanism with the following sequence of steps is proposed for the catalytic oxidation of SO_2:

(a) diffusion of the reactants SO_2 and O_2 to the catalyst surface.
(b) adsorption of the reactants on the surface.
(c) chemical reaction (oxidation) on the surface.
(d) desorption of the product SO_3 from the surface.
(e) diffusion of the product SO_3 from the surface.

Because steps (a) and (e) are usually very fast, step (b), step (c), or step (d) may be rate determining for this mechanism. The literature covering the mechanism of SO_2 catalysis by platinum in automotive applications is quite limited.[5-12] Consequently, we must turn to industrial heterogeneous catalysis experience in order to formulate a general rate expression for the catalytic oxidation of SO_2. The rate equation of Uyehara - Watson is perhaps the best industrial formulation with respect to generality, mathematical depiction, and experimental data representation.[13] Their rate equation is first order with respect to SO_2 partial pressure and is proportional to the square root of oxygen partial pressure. In addition, they define the rate determining step as the surface reaction between adsorbed O_2 and adsorbed SO_2. Hammerle and Truex[10] in their recent flow reactor investigations of the kinetics of SO_2 oxidation for various automotive catalyst compositions have used a similar expression, approximating that the rate of sulfur dioxide oxidation is first order in SO_2. This approximation, equating the automotive catalytic SO_2 oxidation rate expression with the industrial SO_2 oxidation rate expression, appears valid.

The quantity of SO_3 formed is influenced by many factors including the concentration of O_2 in the exhaust, the mass flow of sulfur through the engine, the type of catalyst, the temperature of the catalyst, and possible reactions of SO_2 and SO_3 with other exhaust constituents. In

addition, the quantity of SO_3 formed is complicated by the problem of sulfur oxide storage/release within the catalyst. That is, investigators have not been able to obtain a chemical mass balance between the sulfur burned in the fuel and the sulfur emitted from the tailpipe in catalyst equipped vehicles. Inherent in these investigations is the assumption that the analytical methodology for SO_2 and sulfate detection[14] is sufficient and accurate. Therefore, the problem of obtaining a sulfur mass balance directly relates to the intra-catalyst storage/release phenomena. Investigators of non-catalyst vehicles have usually been able to obtain credible sulfur mass balances.[8] Consequently, we need to focus our attention upon the intra-catalyst storage/release phenomena in order to better understand the complicated mechanism(s) of sulfate formation and emission.

In the exhaust system we have thus far noted that SO_2 may be catalytically oxidized to SO_3. These two gaseous sulfur oxides, SO_2 and SO_3, may react with other exhaust gas constituents and, in addition, react with the aluminum oxide catalyst substrate material and with the iron contained in the engine and exhaust system. The sulfur oxide reactions with the aluminum oxide catalyst substrate material are referred to as the intra-catalyst storage/release phenomena and are illustrated in Figure 2. Reactions (5) and (6) with iron oxide are chemically similar and are thermodynamically favorable at temperatures below 450°C.[15-17] Below 450°C, sulfur oxide storage occurs with iron sulfite/sulfate as the product. As the temperature increases above 450°C, sulfur oxide is released according to reaction (7).[18,19]

(5) $3SO_2 + Fe_2O_3 \longrightarrow Fe_2(SO_3)_3$ Sulfition process

(6) $3SO_3 + Fe_2O_3 \longrightarrow Fe_2(SO_4)_3$ Sulfation process

(7) $2Fe_2(SO_4)_3 \xrightarrow{\Delta} 2Fe_2O_3 + 6SO_2 + 3O_2$ Sulfur oxide release

Consequently, depending upon the temperature and sulfur oxide concentration, sulfation is possible over a large portion of the exhaust system. Those zones in the exhaust system in which the temperature varies may therefore either store or release sulfur oxides.

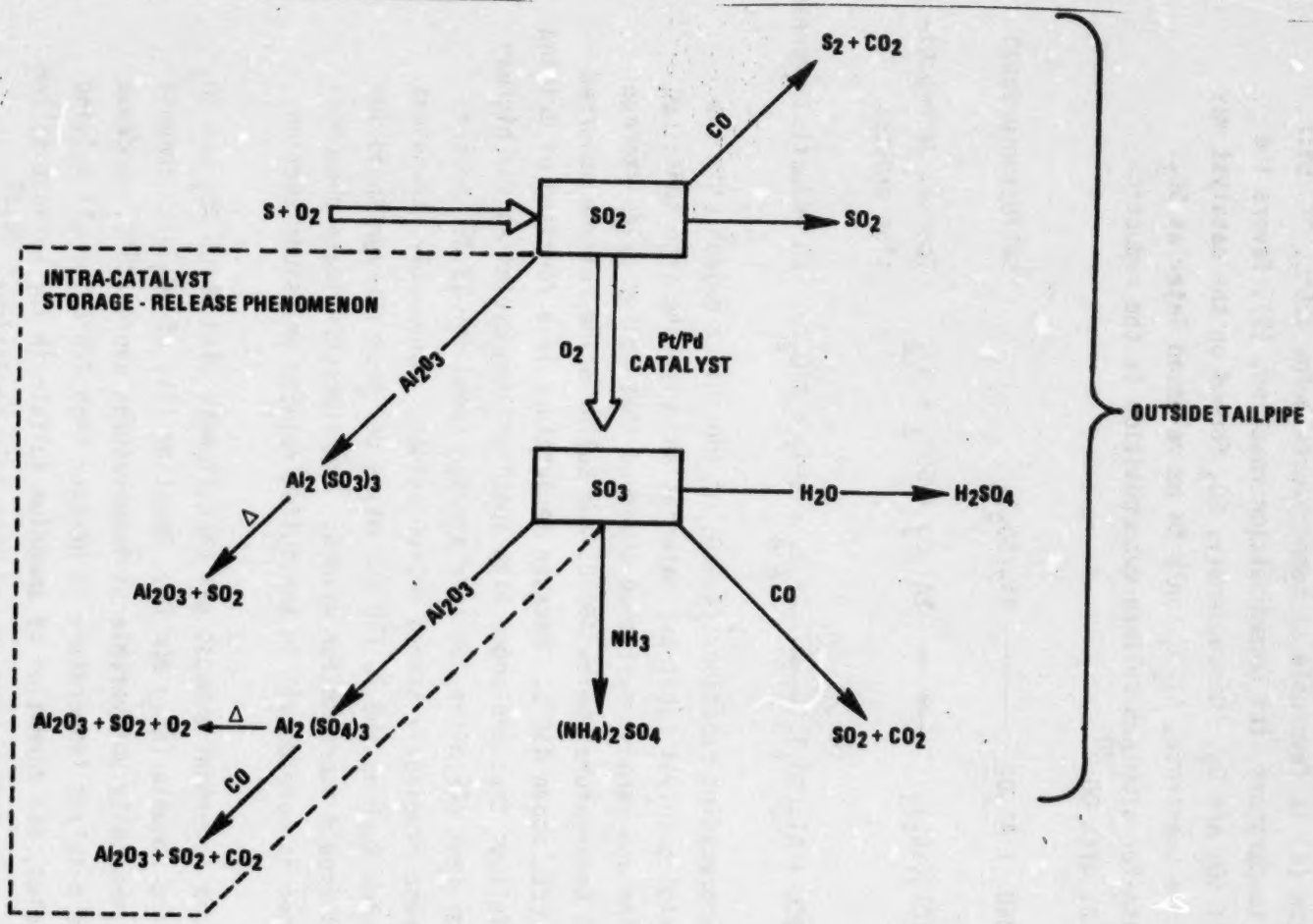

Figure 2. Combustion reactions of sulfur related compounds in the exhaust.

A similar reaction mechanism is proposed for sulfur oxide reaction with the aluminum oxide catalyst substrate. Thermodynamic data indicate that reaction (8) is favorable at temperatures below 425°C. [20] With increasing temperature, the decomposition reaction, (9), favors the formation of SO_2 and O_2. Consequently, SO_3 formed on the catalyst may react with the substrate, Al_2O_3, only to be released later as SO_2. Another route for aluminum sulfate decomposition is the reduction reaction (10) with CO.[20]

(8) $3SO_3 + Al_2O_3 \longrightarrow Al_2(SO_4)_3$ Sulfation process

(9) $2Al_2(SO_4)_3 \xrightarrow{\Delta} 2Al_2O_3 + 6SO_2 + 3O_2$ Thermal decomposition process

(10) $3CO + Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3SO_2 + 3CO_2$ CO reduction process

In the preceding reactions (4 -10) of the sulfur oxides with the aluminum oxide catalyst substrate material and with the iron contained in the engine and exhaust system we observed that sulfur oxide storage occurred at temperatures below 450°C, and sulfur oxide release occurred at temperatures above 450°C. Because temperature is a function of driving cycle, it follows that prolonged high speed driving cycles as the highway fuel economy test (48 miles per hour average speed for 12.25 minutes) should release previously stored sulfur oxides. Conversely, transient driving cycles such as the 75 FTP (22 miles per hour average speed for 31 minutes) should store sulfur oxides. The storage/release phenomena are discussed in more detail in the sulfur related emissions section.

The most important exhaust gas constituents with which SO_2 and SO_3 can react are ammonia (NH_3) and CO. Reaction (11) of SO_3 with ammonia is thermodynamically unfavorable at temperatures above 225°C. Because the average catalyst temperature is greater than 225°C for all driving cycles studied, the formation of ammonium sulfate in the exhaust system could occur only during warm-up and some idle conditions. [20,21] In addition, it is more probable that ammonia would be catalytically

oxidized over platinum according to reaction (12) before reaction with SO_3 could occur.[22] The carbon monoxide reductions of SO_3 to SO_2 (13) and SO_2 to elemental sulfur (14) are thermodynamically favorable but kinetically limited.

(11) $2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4$		Sulfation process
(12) $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$		Catalytic oxidation process
(13) $SO_3 + CO \longrightarrow SO_2 + CO_2$		CO reduction process
(14) $2SO_2 + 4CO \longrightarrow S_2 + 4CO_2$		CO reduction process

In summary, the possibility exists for reaction of sulfur oxides with both exhaust gas constituents on the one hand and, on the other, with the catalyst substrate material and iron contained in the engine and exhaust system. Reactions (11-14) with exhaust gas constituents are generally thermodynamically favorable but kinetically limited. Reactions (5-10) with Al_2O_3 and Fe_2O_3 are thermodynamically and kinetically more favorable; hence their occurrence is more probable.

SECTION 4

EXPERIMENTAL

The experimental apparatus used consisted of (1) seven separate automobiles tested on four separate sulfur level fuels, (2) chassis dynamometer test equipment, (3) a dilution tube constant volume sampling system (CVS), and (14) the analytical instrumentation necessary to perform the chemical analyses.

Table 1 describes the characteristics of the seven test vehicles. With the exception of the Honda CVCC, all were 1975 production vehicles

Table 1. DESCRIPTION OF 1975 MODEL YEAR VEHICLES

Make, model	Inertia weight, lb	Engine	Exhaust emission control system
Chevrolet Impala	5000	350 CID V-8, 2 bbl	GM/AC Catalyst (Pellet), EGR.
Chevrolet Nova	4000	250 CID 6, 1 bbl	GM/AC Catalyst (Pellet), EGR.
Plymouth Fury	5000	318 CID V-8, 2 bbl	Universal Oil Products Catalyst (Monolith), EGR.
Plymouth Scamp	4000	225 CID 6, 1 bbl	Universal Oil Products Catalyst (Monolith), EGR.
Ford Granada	4000	302 CID V-8, 2 bbl	Matthey - Bishop Catalyst (Monolith), EGR, Air Pump.
Ford Torino	4500	351 CID V-8, 2 bbl	Engelhard Catalyst (Monolith), EGR, Air Pump.
Honda CVCC	2000	91 CID 4, 3 bbl	Stratified Charge Engine

and were leased locally. The lease vehicles had acquired a maximum of 800 road miles prior to our lease and were driven on unleaded gasoline only. The Honda CVCC was a 1975 prototype designed to meet the 1975 statutory emissions standards of 0.41 g/mile HC, 3.4 g/mile CO, and 3.1 g/mile NO_x. All were tuned to manufacturers' specifications and checked for exhaust leaks prior to testing. Each vehicle was conditioned via highway driving on its particular test fuel for a minimum road distance of 250 miles prior to chassis dynamometer testing.

The vehicles were tested using both the 1975 Federal Test Procedure (75 FTP) and the Highway Fuel Economy Test (HWFET) procedure as described in the Federal Register.[23] Cycles were manually driven on a Clayton CT-50 water brake dynamometer with direct drive flywheels. The dynamometer had been calibrated for load via the Federal Register coast down procedure prior to the vehicular test sequences. A standard 5000 CFM fan, as specified in the Federal Register, was used to cool the vehicles. No supplemental fan was used to cool the vehicle catalyst during testing. Vehicle exhaust samples were accumulated using a conventional Scott constant volume sampling system arranged for 6 bag sampling, with a total exhaust plus dilution air flow rate of 406.9 ACFM. This system was flow calibrated by the propane injection method described in the Federal Register.

Gaseous exhaust emission analyses were made using Federal Register specified instrumentation for hydrocarbons, CO, NO_x, and CO_2. The total hydrocarbons in bag samples were determined using a Beckman 400 flame ionization detector. Individual C_1 - C_{10} detailed hydrocarbons were determined by computer operated gas chromatographic analyses of the bag samples. The results have previously been reported.[24] Carbon monoxide and CO_2 were determined in bag samples using a Philco-Ford prototype gas filter correlation spectrometer.[25] Oxides of nitrogen (NO and NO_2) were determined in bag samples using a Thermo-Electron model 10A Chemiluminescence Analyzer. These routine gas analyzers were mounted in an instrument train conforming to Federal Register specifications and were calibrated using span gases that had been checked against NBS

certified standard reference material gases. All calculations for gaseous emission rates (HC, CO, NO_x, CO_2) and fuel economy (miles-per-gallon or mpg) were made according to Federal Register specifications. Sulfur dioxide (SO_2) was measured in the dilute exhaust by pulling the gaseous sample through heated (100°C) stainless steel lines into a 50 ml bubble-breaking type fritted glass absorber containing 25 ml of tetrachloromercurate solution. Sulfur dioxide was then determined by the West-Gaeke method [26] using a modified Technicon Automated Air Monitor IV instrument.

Particulate emissions were measured using a cylindrical stainless steel dilution tube sampling system, 18 inches in diameter and 15 feet long; it was equipped with four 0.900 inch internal diameter stainless steel sampling probes operating isokinetically at 1.06 CFM. The dilution tube sampling system is illustrated in Figure 3. Tunnel and probe losses were less than 1 percent of the collected particulate. Routine particulate matter samples were collected on either 47-mm fluorocarbon type filters (Fluoropore type FA from Millipore Corporation) having a 1 micron nominal porosity, or on Gelman type "A" glass fiber filters. In usual practice, three probes employed the Fluoropore filters and one probe employed the glass fiber filter. Particulate samples were obtained over the 31 minute active portion of the 75 FTP and over the entire Highway Fuel Economy Test. Filter weighings were performed on a microbalance to the nearest 2 micrograms after 48 hours conditioning at 50% relative humidity and 25°C. Sulfate analyses were performed upon the filters using the automated barium chloranilate method.[27] X-ray fluorescence analysis for trace metals was performed using a computer operated 17 channel Siemens analyzer.[(28)] Elemental analyses for percent carbon and hydrogen were performed upon the glass fiber filters using a Perkin-Elmer automated combustion analyzer.

The gasoline used in all experiments was an unleaded reference test fuel. Operation with this fuel was satisfactory for all test vehicles. The sulfur level of the reference or base fuel was 0.020 weight percent sulfur. Sulfur levels were increased by doping the base fuel with

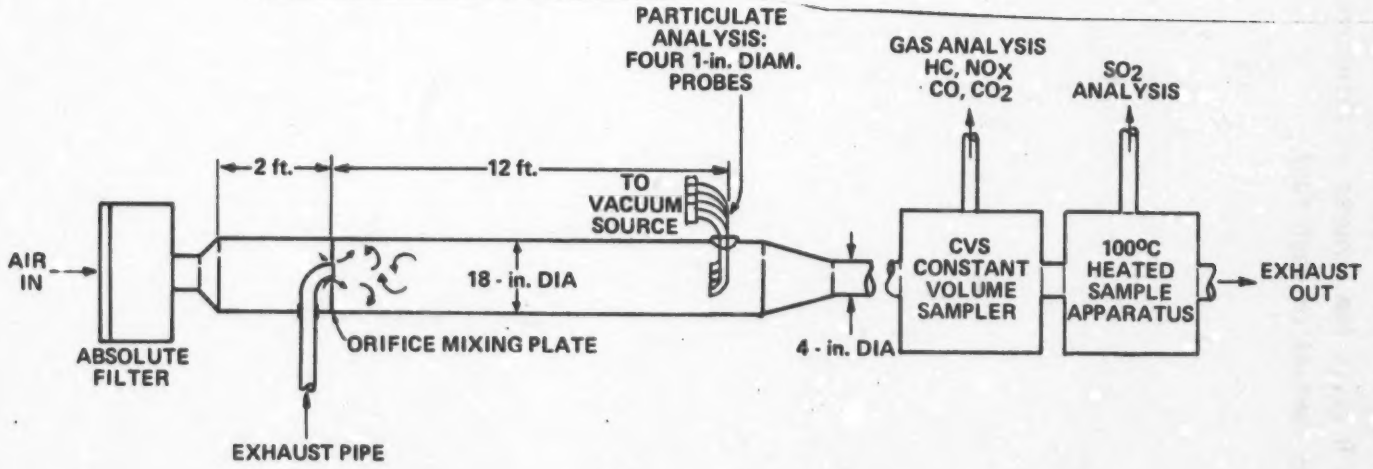

Figure 3. Sampling system.

reagent grade Thiophene, C_4H_4S, from Eastman Kodak Company, Eastman Organic Chemicals, Rochester, New York. Appendix A lists the properties of the test fuel; appendix B lists the amounts of thiophene added and the analysis for the sulfur content of each fuel.

SECTION 5

RESULTS AND DISCUSSION

GASEOUS EMISSIONS

Table 2 lists the gaseous emissions data for the test vehicles for the 1975 FTP and the 1975 HWFET. All vehicles tested met the level of the 1975 interim emission standards of 1.5 g/mile HC, 15 g/mile CO, and 3.1 g/mile NO_x. The Honda CVCC, the only non-catalyst vehicle tested in these experiments, gave the lowest overall emissions for HC, CO, and NO_x. In fact, the Honda met the level of the proposed 1977 standard of 0.41 g/mile HC, 3.4 g/mile CO, and 2.0 g/mile NO_x. Of the six domestic production vehicles, the Chevrolets gave the lowest overall emissions, followed by the Ford vehicles and the Plymouth vehicles, respectively. In terms of fuel economy, the Honda CVCC, as expected, achieved the highest mileage in both the 75 FTP and HWFET. Of the domestic production vehicles, the Plymouths achieved the best overall mileage, followed closely by the Chevrolets and the Ford vehicles, respectively.

Table 2-a. 1975 FTP GASEOUS EMISSIONS (grams/mile)

Vehicle	N	HC	CO	NO_x	CO_2	Fuel economy, mpg
Impala	9	0.281	4.213	1.933	635	13.63
Nova	10	0.284	3.189	1.786	522	16.55
Fury	9	0.558	5.393	2.624	675	12.80
Scamp	9	0.716	13.042	1.364	488	17.02
Granada	25	0.581	4.665	1.060	566	15.24
Torino	30	1.110	4.123	1.492	605	14.29
Honda	29	0.245	2.890	1.270	366	23.56

Table 2-b. 1975 HWFET GASEOUS EMISSIONS (grams/mile)

Vehicle	N	HC	CO	NO_x	CO_2	Fuel economy, mpg
Impala	9	0.119	1.815	2.496	435	19.89
Nova	9	0.126	0.399	1.392	387	22.44
Fury	8	0.155	0.685	3.198	451	19.29
Scamp	7	0.420	1.284	1.793	341	25.41
Granada	25	0.300	0.873	1.342	457	19.17
Torino	30	0.543	2.436	2.077	478	18.06
Honda	25	0.058	0.853	1.494	300	28.85

With the stock spark timing it was noticed that the Chevrolet and Plymouth vehicles would ping under mild acceleration. Therefore, the spark timing of the Chevrolet Impala and Nova and the Plymouth Fury and Scamp was retarded 5° for some 75 FTP runs. This experiment was performed for two reasons: first, to check upon the emission levels and fuel economy with the retarded spark, and second, to check upon vehicle driveability and the level of "pinging" with the retarded spark. The results are listed in Table 3 and in all cases there was an overall 6% decrease in fuel economy associated with the retarded spark. Both Chevrolets showed an increase in HC and CO emission levels and a decrease in the NO_x emission level. Both Plymouths exhibited a decrease in observed HC emissions and an increase in CO emissions. The Plymouth Fury emitted 8% less NO_x under the retarded spark condition while the Plymouth Scamp emitted 9% more NO_x under identical conditions. The driveability of all vehicles with the retarded spark remained essentially the same as when tested with the stock spark. The "pinging" associated with the stock spark under mild acceleration did disappear with the 5° spark retard. Thus it appears that one could retard the spark timing approximately 5° in order to decrease the "pinging" arising from use of currently available unleaded gasolines. However, the penalty associated with this operation is decreased fuel economy and an increase in regulated emissions.

Table 3. COMPARISON OF 1975 FTP GASEOUS EMISSIONS FROM VEHICLE TIMED AT STOCK SPARK IGNITION WITH VEHICLE TIMED AT 5° RETARDED SPARK FROM MANUFACTURER SPECIFICATIONS

Vehicle	Spark	1975 FTP Gaseous Emissions, grams/mile					
		N	HC	CO	NO_x	CO_2	Fuel economy, mpg
Impala	Stock	9	0.281	4.213	1.993	635	13.63
Impala	5° Retard	4	0.344	9.127	1.604	700	12.31
Nova	Stock	10	0.284	3.189	1.786	522	16.55
Nova	5° Retard	4	0.313	5.718	1.587	545	15.80
Fury	Stock	9	0.558	5.393	2.624	675	12.80
Fury	5° Retard	5	0.445	6.841	2.421	702	12.27
Scamp	Stock	9	0.716	13.042	1.364	488	17.02
Scamp	5° Retard	5	0.641	13.780	1.493	548	15.75
Average Difference (5° Retard/Stock)	Chevrolets:		+16%	+ 98%	-15%	+7%	-7%
	Plymouths:		- 15%	+16%	+ 1%	+8%	-6%

SULFUR-RELATED EMISSIONS

The sulfur-related emissions listed in Tables 4-10 detail the fuel sulfur levels, the SO_2 emission rates in grams per mile, the SO_2 sulfur balances, the particulate emission rates in milligrams per mile, the sulfate emission rates in milligrams per mile, the sulfate percent of the particulate matter, the SO_4 sulfur balances, and the total sulfur balances for the 75 FTP and the HWFET for the seven test vehicles studied. Table 11 lists the SO_2 linear regression analysis, Table 12 lists the SO_4 linear regression analysis, and Table 13 lists the particulate matter linear regression analysis, all as a function of fuel sulfur level. After initial highway conditioning on a particular test fuel, the driving schedule involved alternating 75 FTP's and HWFET's for each vehicle. The Chevrolet and Plymouth vehicles' sequential order of fuel sulfur level during testing was 0.087, 0.020, 0.036, and 0.053 weight percent sulfur. The Ford and Honda vehicles' sequential order of fuel sulfur level during testing was 0.020, 0.041, 0.059, and 0.084 weight percent sulfur. Consequently, there is a substantial amount of data and analyses presented for the seven test vehicles in the two driving cycles using four different sulfur level fuels ranging in value from 0.020 to 0.087 weight percent sulfur.

The SO_2 emission rates and SO_2 sulfur balances vary considerably. They are dependent upon the type of vehicle/catalyst, the fuel sulfur level, and the driving cycle. For example, the pellet catalyst equipped Chevrolets (Nova and Impala) are the lowest SO_2 emitters in the 75 FTP, and, conversely, are the highest SO_2 emitters in the HWFET. This is expected due to the nature of the pellet catalyst which, because of its large surface and alumina contact area, has a greater capacity to store sulfur oxides than do monolithic catalysts. As mentioned previously, sulfur oxide storage tends to occur during low speed/temperature driving modes as the 75 FTP, while sulfur oxide release tends to occur during high speed/temperature driving modes as in the HWFET. The pellet catalyst's SO_2 emission rate supports this mechanism. The correlation coefficients

from the linear regression analysis in Table 11 for the 75 FTP ranged in value from 0.962 to 0.997 (average 0.984 ± .012) indicating excellent linear association of SO_2 emission rate with fuel sulfur level. The regression slopes ranged in value from a high of 3.918 (Ford Granada) to a low of 0.575 (Chevrolet Nova). The order of decreasing FTP SO_2 emission rate was Fury > Granada > Torino > Honda > Scamp > Impala > Nova. The correlation coefficients for the HWFET ranged in value from 0.899 to 0.996 (average 0.965 ± .033) again indicating very good linear association of SO_2 emission with fuel sulfur level. As expected, the regression slopes were greater in the HWFET than in the 75 FTP and ranged in value from a high of 5.584 (Chevrolet Nova) to a low of 1.776 (Honda). The order of decreasing HWFET SO_2 emission rate was Impala > Nova > Torino > Granada > Scamp > Honda > Fury.

The SO_4 emission rates and SO_4 sulfur balances vary considerably also, depending on the type of vehicle/catalyst, on the fuel sulfur level, and on the driving cycle. The correlation coefficients from the linear regression analysis in Table 12 for the 75 FTP ranged in value from 0.674 to 0.990 (average 0.909 ± .116) indicating good linear association of SO_4 emission with fuel sulfur level. The regression slopes ranged in value from a high of 163.369 (Ford Torino) to a low of 15.086 (Honda). The order of decreasing 75 FTP SO_4 emission rate was Torino > Granada > Fury > Nova > Scamp > Impala > Honda. The correlation coefficients for the HWFET ranged in value from 0.959 to 0.996 (average 0.976 ± .017) indicating very good linear association of SO_4 emission with fuel sulfur level. As usual, the regression slopes were greater in the HWFET and ranged in value from a high of 1336.073 (Chevrolet Nova) to a low of 81.346 (Honda). The order of decreasing HWFET SO_4 emission rate was Torino > Granada > Nova > Fury > Impala > Scamp > Honda.

The particulate emission rate data was likewise variable depending on the type of vehicle/catalyst, on the fuel sulfur level, and on the driving cycle. The correlation coefficients from the linear regression analysis in Table 13 for the 75 FTP ranged in value from 0.164 to 0.994 (average 0.788 ± .285) indicating fair linear association of particulate

emission with fuel sulfur level. The regression slopes ranged in absolute value from a high of 909.846 (Ford Torino) to a low of 4.607 (Honda). The Chevrolet Nova in the 75 FTP gave a correlation coefficient of 0.593 and a negative regression slope of -611.377 indicating that its particulate emissions decreased with increasing fuel sulfur level. This anomaly can perhaps be explained by the conditioning of the vehicle/catalyst prior to its arrival for testing at our EPA facility, and by the fact that it had been tested on 0.087 weight percent sulfur fuel prior to testing on the 0.020 weight percent sulfur fuel which gave the greatest particulate emission rate. The Honda 75 FTP particulate emission rate was constant at 5.1 ± 0.8 milligrams per mile, hence its 0.164 correlation coefficient. With the exception of the Nova and the Honda in the 75 FTP, all vehicle particulate emission patterns conformed to normal behavior. The order of decreasing 75 FTP particulate emission rate was Torino > Fury > Granada > Nova > Impala > Scamp > Honda. The correlation coefficients for the HWFET ranged in value from 0.881 to 0.999 (average 0.966 ± .040) indicating very good linear association of particulate emission with fuel sulfur level. As expected, the regression slopes were greater in the HWFET and ranged in value from a high of 2303.632 (Chevrolet Nova) to a low of 148.419 (Honda). The order of decreasing HWFET particulate emission rate was Torino > Nova > Granada > Fury > Impala > Scamp > Honda. The sulfate percent of the particulate matter varied from 4.2 to 55.1% of the particulate matter (average 23.0 ± 14.5%) for all seven vehicles in the 75 FTP and varied from 25.0 to 69.0% (average 50.3 ± 8.9%) in the HWFET. Thus approximately one half of the HWFET particulate matter was sulfate, while approximately one quarter of the 75 FTP particulate matter was sulfate. The total sulfur balances presented in Tables 4-10 indicate that HWFET sulfur balances were usually greater than 100%, ranging from a low of 87% (Plymouth Fury) to a high of 170% (Chevrolet Impala). In contrast, sulfur balances were less in the 75 FTP, ranging from a low of 14% (Chevrolet Nova) to a high of 109% (Honda).

Table 14 summarizes the rankings of the vehicle SO_2, particulate matter, and SO_4 emission rates. The vehicle with the greatest particulate and SO_4 emission rate in both the 75 FTP and the HWFET was the air pump equipped Ford Torino with the Engelhard monolith. The second greatest

SO_4 emitter in the 75 FTP and HWFET was the air pump equipped Ford Granada with the Matthey-Bishop monolith. The addition of excess air resulting in a 4% to 7% tailpipe oxygen level apparently enhances the kinetic rate of oxidation of SO_2 to SO_3; hence, the greater sulfate emission rates for air pump equipped vehicles. The Chevrolet vehicles with the GM/AC pellet catalysts were the lowest SO_2 emitters and, with the exception of the Honda and Plymouth Scamp were also the lowest emitters of SO_4 and particulate matter during the 75 FTP. This result is not surprising due to the large storage capacity of the pellet catalyst. During the HWFET, however, the Chevrolets were the greatest SO_2 emitters, the Nova the third greatest SO_4 emitter and the Impala the fifth greatest SO_4 emitter. The Plymouth vehicles were equipped with the Universal Oil Products monolithic catalysts. In the 75 FTP, the Fury ranked first, second, and third in SO_2, particulate matter, and SO_4 emissions respectively, while the Scamp ranked fifth, sixth, and fifth respectively. In the HWFET, the Fury ranked seventh, fourth, and fourth while the Scamp ranked fifth, sixth, and sixth in SO_2, particulate matter, and SO_4 emission respectively. The non-catalyst Honda emitted the least particulate matter and the least SO_4 in both the 75 FTP and HWFET. Overall, the Honda had the lowest regulated gaseous emissions and the lowest sulfur-related emissions.

NON-SULFATE PARTICULATE MATTER

The fuel parameter exerting the greatest influence over total particulate emissions was the fuel sulfur level. Tables 4-10 describe the particulate emission rates in milligrams per mile as a function of fuel sulfur for both the 75 FTP and the HWFET. Table 13 describes the linear regression analysis for the particulate emission rate as a function of fuel sulfur level. The correlation or measurement of linear association between the particulate emission rate and the fuel sulfur is especially good for the six catalyst vehicles. Excepting the Chevrolet Nova, which had an unusually high particulate emission rate using 0.020% sulfur fuel, the correlation coefficients for the five other catalyst vehicles in the 75 FTP ranged in value from 0.904 to 0.994 (average $0.958 \pm .038$). In the HWFET the correlation coefficients ranged in

Table 4. CHEVROLET IMPALA SO_2, SO_4, AND PARTICULATE EMISSIONS

75 FTP Results

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 particulate	Fuel S as SO_4	Total sulfur balance
3	0.020	0.017	18.7%	4.5	0.3	6.7	0.3%	0.190
3	0.036	0.043	29.3%	5.4	0.6	11.1	0.3%	0.296
3	0.053	------	------	7.8	1.2	15.4	0.4%	------
6	0.087	0.168	49.7%	9.4	1.6	17.0	0.3%	0.500

HWFET Results

3	0.020	0.070	125.0%	3.1	1.4	45.2	1.7%	1.267
3	0.036	0.110	110.0%	14.8	7.0	47.3	5.0%	1.150
3	0.053	0.378	257.1%	21.6	11.8	54.6	5.5%	2.626
6	0.087	0.414	171.8%	32.4	17.4	53.7	3.3%	1.751

Table 5. CHEVROLET NOVA SO_2, SO_4, AND PARTICULATE EMISSIONS

75 FTP Results

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 / Particulate	Fuel S as SO_4	Total sulfur balance
3	0.020	0.002	2.8%	73.9	3.1	4.2	3.2%	0.060
3	0.036	0.022	18.2%	16.4	0.8	4.9	0.4%	0.186
3	0.053	0.023	12.9%	9.2	1.1	12.0	0.4%	0.133
7	0.087	0.044	5.5%	21.3	6.6	31.0	1.6%	0.171

HWFET Results

3	0.020	0.015	33.3%	7.2	1.8	25.0	4.3%	0.376
3	0.030	0.090	101.1%	25.3	11.5	45.5	9.8%	1.109
3	0.053	0.199	153.1%	42.0	21.4	51.0	10.5%	1.636
6	0.087	------	------	159.4	89.9	56.4	32.2%	------

Table 6. PLYMOUTH FURY SO_2, SO_4, AND PARTICULATE EMISSIONS

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 Particulate	Fuel S as SO_4	Total sulfur balance
75 FTP Results								
3	0.020	0.060	63.2%	5.4	1.1	20.4	0.9%	0.641
3	0.036	0.139	88.5%	8.5	1.9	22.4	0.8%	0.893
3	0.053	0.209	90.1%	15.6	4.1	26.3	1.2%	0.913
6	0.087	0.290	79.2%	35.0	19.3	55.1	3.5%	0.827
HWFET Results								
3	0.020	0.047	75.8%	10.2	5.5	53.9	6.7%	0.825
3	0.036	0.086	81.9%	16.7	9.7	58.1	6.5%	0.884
3	0.053	0.112	72.7%	38.1	20.6	54.1	9.5%	0.822
5	0.087	0.200	82.0%	126.1	71.3	56.5	14.1%	0.961

Table 7. PLYMOUTH SCAMP SO_2, SO_4, AND PARTICULATE EMISSIONS

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 / Particulate	Fuel S as SO_4	Total sulfur balance
75 FTP Results								
3	0.020	0.017	25.4%	2.5	0.2	8.0	0.2%	0.256
3	0.036	0.073	64.0%	4.1	1.3	31.7	0.8%	0.648
3	0.053	0.131	78.4%	3.2	0.7	21.9	0.3%	0.787
6	0.087	0.186	69.9%	8.8	2.0	22.7	0.5%	0.704
HWFET Results								
3	0.020	0.042	87.5%	2.7	1.8	66.7	2.1%	0.896
3	0.036	0.117	140.0%	8.9	4.4	49.4	3.5%	1.435
3	0.053	0.168	118.0%	14.2	9.8	69.0	6.2%	1.242
4	0.087	0.209	113.6%	22.5	14.3	63.6	5.0%	1.186

Table 8. FORD GRANADA SO_2, SO_4, AND PARTICULATE EMISSIONS

75 FTP Results

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 / Particulate	Fuel S as SO_4	Total sulfur balance
7	0.020	0.048	65.8%	6.9	1.1	15.9	1.0%	0.668
8	0.041	0.111	76.0%	10.9	3.9	35.8	1.8%	0.778
5	0.059	0.188	87.0%	10.9	5.0	45.9	1.5%	0.885
5	0.084	0.296	96.7%	20.6	8.7	42.2	1.9%	0.986
				HWFET Results				
6	0.020	0.089	153.4%	19.5	8.6	44.1	11.2%	1.646
9	0.041	0.112	94.9%	35.6	18.4	51.7	10.5%	1.054
5	0.057	0.193	110.9%	39.2	18.5	47.2	7.1%	1.180
5	0.084	0.272	110.6%	56.1	26.4	47.1	7.2%	1.178

Table 9. FORD TORINO SO_2, SO_4, AND PARTICULATE EMISSIONS

75 FTP Results

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 Particulate	Fuel S as SO_4	Total sulfur balance
8	0.020	0.067	83.8%	19.2	3.8	19.8	3.2%	0.870
10	0.041	0.101	64.3%	33.8	13.8	40.8	5.8%	0.701
6	0.059	0.160	70.2%	50.0	21.2	42.4	6.2%	0.764
6	0.084	0.226	71.1%	77.2	33.7	43.7	7.0%	0.781

HWFET Results

6	0.020	0.084	133.3%	33.5	15.4	46.0	16.3%	1.496
9	0.041	0.109	89.3%	66.2	34.1	51.5	18.7%	1.080
6	0.059	0.195	108.9%	97.4	43.2	44.4	16.1%	1.250
5	0.084	0.249	95.4%	135.1	62.7	46.4	16.1%	1.115

Table 10. HONDA CVCC SO_2, SO_4, AND PARTICULATE EMISSIONS

75 FTP Results

No. of tests	Fuel % sulfur level	SO_2, g/mile	Fuel S as SO_2	Particulate, mg/mile	SO_4, mg/mile	% SO_4 / Particulate	Fuel S as SO_4	Total sulfur balance
8	0.020	0.071	127.7%	5.2	0.2	4.6	0.3%	1.280
9	0.041	0.093	98.9%	5.2	0.4	7.7	0.3%	0.992
6	0.059	0.134	96.4%	4.0	0.5	12.5	0.2%	0.996
6	0.084	0.226	112.4%	5.8	1.2	20.7	0.4%	1.128

HWFET Results

6	0.020	0.072	189.5%	13.3	4.6	34.6	8.2%	1.977
7	0.041	0.087	108.8%	13.4	6.3	47.0	5.3%	1.141
6	0.059	0.116	103.6%	14.9	8.2	55.0	4.9%	1.085
6	0.084	0.185	114.2%	22.9	9.7	42.4	4.0%	1.182

Table 11. SO_2 LINEAR REGRESSION ANALYSIS

SO_2 (g/mile) = a + b (FUEL WEIGHT % SULFUR)

75 FTP

Vehicle	a = Intercept	b = Slope	R = Correlation coefficient
Impala	-0.034	2.302	0.997
Nova	-0.005	0.575	0.962
Fury	0.010	3.364	0.983
Scamp	-0.020	2.490	0.979
Granada	-0.039	3.918	0.996
Torino	0.008	2.552	0.992
Honda	-0.004	2.593	0.980

HWFET

Vehicle	a = Intercept	b = Slope	R = Correlation coefficient
Impala	-0.030	5.881	0.899
Nova	-0.102	5.584	0.992
Fury	0.001	2.254	0.996
Scamp	0.015	2.405	0.953
Granada	0.014	3.000	0.978
Torino	0.019	2.748	0.977
Honda	0.024	1.776	0.962

Table 12. SO_4 LINEAR REGRESSION ANALYSIS

SO_4 (mg/mile) = a + b (FUEL WEIGHT % SULFUR)

75 FTP

Vehicle	a = Intercept	b = Slope	R = Correlation coefficient
Impala	- 0.049	19.879	0.975
Nova	- 0.173	62.713	0.674
Fury	- 7.152	280.648	0.941
Scamp	- 0.063	22.713	0.839
Granada	- 1.176	114.724	0.991
Torino	- 5.507	463.369	0.999
Honda	- 0.194	15.086	0.942

HWFET

Vehicle	a = Intercept	b = Slope	R = Correlation coefficient
Impala	- 2.043	233.522	0.982
Nova	-34.318	1336.073	0.959
Fury	-22.943	1014.656	0.959
Scamp	- 1.812	191.579	0.984
Granada	4.877	256.820	0.958
Torino	2.079	721.003	0.996
Honda	3.051	81.346	0.994

Table 13.

PARTICULATE MATTER LINEAR REGRESSION ANALYSIS

PARTICULATE (mg/mile) = a + b (FUEL WEIGHT % SULFUR)

75 FTP

Vehicle	a = Intercept	b = Slope	R = Correlation coefficient
Impala	3.051	75.992	0.975
Nova	60.157	- 611.377	0.593
Fury	- 6.199	455.587	0.984
Scamp	0.258	89.636	0.904
Granada	2.095	200.587	0.904
Torino	- 1.352	909.846	0.994
Honda	4.815	4.607	0.164

HWFET

Vehicle	a = Intercept	b = Slope	R = Correlation coefficient
Impala	- 2.563	419.150	0.979
Nova	-54.354	2303.632	0.961
Fury	-40.133	1794.049	0.961
Scamp	- 2.165	290.607	0.994
Granada	9.856	543.993	0.984
Torino	1.574	1597.561	0.999
Honda	8.556	148.419	0.881

Table 14. OVERALL RANKING BY SO_2, PARTICULATE, AND SO_4 EMISSION RATES

75 FTP

Vehicle	SO_2 emission	Particulate emission	SO_4 emission
Impala	6	5	6
Nova	7	4	4
Fury	1	2	3
Scamp	5	6	5
Granada	2	3	2
Torino	3	1	1
Honda	4	7	7

HWFET

Vehicle	SO_2 emission	Particulate emission	SO_4 emission
Impala	1	5	5
Nova	2	2	3
Fury	7	4	4
Scamp	5	6	6
Granada	4	3	2
Torino	3	1	1
Honda	6	7	7

value from 0.961 to 0.999 (average 0.980 ± .016) for the six catalyst cars. The Honda CVCC particulate emission rate in the 75 FTP was constant as 5.1 ± 0.8 mg/mile, while its particulate emission behavior in the HWFET was similar to that of the catalyst vehicles with a correlation coefficient of 0.881. The Honda was generally the lowest particulate emitter in both the 75 FTP and the HWFET for most fuels studied.

As expected, a great portion of the particulate matter was sulfate and its associated bound water. The sulfate percent of the particulate matter averaged 50.3 ± 8.9% for all seven test vehicles in the HWFET and 23.0 ± 14.5% in the 75 FTP. In other words, at least one half of the particulate matter was sulfate in the HWFET runs decreasing to a quarter of the particulate matter being sulfate in the FTP runs.

The non-sulfate portion of the particulate matter may be divided into two general categories: organic matter and inorganic matter. Organic matter was determined by elemental combustion analyses performed upon Gelman type A glass fiber filters. These analyses, reporting percent carbon and hydrogen, indicated that organic material comprised from a minimum of ∿2% to a maximum of ∿35% of the total particulate mass for the six catalyst vehicles. In the case of the Honda CVCC, the organic material material composed ∿23% of the total particulate mass in the 75 FTP and ∿51% of the total particulate mass in the HWFET. No organic extractions have been performed upon the particulate samples in order to clarify the composition of the organic material. Further investigation into this area is warranted.

The remaining non-sulfate, non-organic particulate matter is of inorganic origin. Accordingly, the following metals were measured by x-ray fluorescence for the seven test vehicles: silicon (Si), cadmium (Cd), aluminum (Al), sulfur (S), magnesium (Mg), potassium (K), zinc (Zn), nickel (Ni), iron (Fe), titanium (Ti), barium (Ba), calcium (Ca), platinum (Pt), and vanadium (V). The elemental carbon, hydrogen and metal emission rates in milligrams per mile are entered in Tables 15-18.

Because x-ray fluorescence does not provide information concerning the combination state of the analyzed metal, it is a reasonable assumption that the metals are combined with other elements in the form of oxidation products.

Elements of prominent concentration in the particulate matter were sulfur, iron, aluminum, zinc and calcium. The other elements detected were present in trace quantities only and appear to follow no pattern with regard to fuel sulfur level or with regard to the driving cycle selected. No platinum was detected in the analyses. With the exception of sulfur, the most prominent element detected in the particulate matter was iron. The iron emission rate for all test vehicles, with the exception of the Honda and the Chevrolets, was greater in the 75 FTP than in the HWFET. Also, the catalyst vehicle iron emission rate was greater than that of the non-catalyst Honda CVCC. The iron presumably arises from engine and exhaust system wear in both catalyst and non-catalyst vehicles. The increase in iron emissions of the catalyst equipped vehicle over the non-catalyst vehicle suggests reaction of the iron and iron oxides on the exhaust system surface with the catalytically produced H_2SO_4. Because steady state operation tends to produce and release previously stored sulfate, one would initially expect the HWFET iron emission rate to be greater than the 75 FTP iron emission rate. However, steady state or cruise operations, although conducive to sulfate production and reaction, are not conducive to detachment of material from exhaust system surfaces. Detachment usually occurs under cyclic vehicle operations - during accelerations and decelerations as in the 75 FTP - hence the reason for 75 FTP iron emissions usually being greater than HWFET iron emissions.

Aluminum was the third most prominent element detected in the particulate matter. As was the case with iron, the aluminum emission rate for all test vehicles with the exception of the Honda, was greater in the 75 FTP than in the HWFET. Also, the catalyst vehicle aluminum emission rates were greater than that of the Honda CVCC, since some attrition of the catalyst substrate Al_2O_3 was expected. The GM/AC pelleted catalysts

were the greatest aluminum emitters, followed by the Engelhard monolith (Ford Torino), the Universal Oil Products Monoliths (Plymouths), and the Matthey-Bishop monolith (Ford Granada).

The fourth and fifth most prominent elements detected in the particulate matter were calcium and zinc respectively. The calcium and zinc emission rates were greater for the non-catalyst Honda than for the other six vehicles, with the exception of the Chevrolets in the case of zinc emissions. The reason for the GM/AC pelleted catalyst-equipped vehicles generating the greatest zinc emission is uncertain. Perhaps the zinc emitted is a corrosion or reaction product of H_2SO_4 with the Chevrolet exhaust system. Similar observations have been reported by Beltzer.[29] In the case of the Honda, the increased calcium and zinc emissions appear derived from lubricating oil consumption. We may determine a mass balance for the particulate matter by assuming that the prominent elements listed in Tables 15-18 are in reality emitted as oxidation products. That is, Al is emitted as Al_2O_3, Fe is emitted as Fe_2O_3, and S is emitted as H_2SO_4 aerosol. Carbon, however, is assumed to be emitted in its elemental form as a carbonaceous product only. Consequently, we may sum the masses of the individual products and compare this resultant sum to the experimental particulate emission rates listed in Tables 4-10. For the six catalyst cars, the sum of the individual products gives 85 ± 19% of the experimental particulate emission rate in the 75 FTP and 66 ± 16% in the HWFET. In the case of the Honda CVCC, the sum of the individual products gives approximately 55% of the experimental particulate emission rate in the 75 FTP and approximately 103% in the HWFET. The overall mass balance for the seven test vehicles was 81 ± 21% in the FTP and 72 ± 20% in the HWFET, and considering the rather simple assumptions used, this gives a fair indication of the chemical composition of the particulate. The particulate material balances are illustrated in Figure 4.

In summary, SO_2, particulate matter, and H_2SO_4 emission rates increased with increasing fuel sulfur for all vehicles. The reproducibility and magnitude of the SO_2, particulate matter, and SO_4 emissions were

greater in the HWFET than in the 75 FTP. The accuracy and magnitude of the emission rates are directly attributable to the characteristics of the driving cycles. The HWFET is essentially a steady state operation at 48 mph covering 10.24 miles in 12.75 minutes while the 75 FTP represents city driving with frequent accelerations and decelerations for a transient type of operation with an average speed of 22 mph covering 11.09 miles in 31 minutes. In addition, the average catalyst temperature is approximately 25% greater during the HWFET than during the 75 FTP. Sulfur oxide storage was observed to occur during the low speed/temperature transient modes (75 FTP) only to be released during the higher speed/temperature modes (HWFET). That is, sulfur oxide storage accounts for total sulfur balances being consistently less than theoretical in the 75 FTP and consistently greater than theoretical in the HWFET. The sulfur oxide storage/release phenomena is also dependent upon the type of catalyst in addition to the type of driving cycle. Pelleted catalysts with their large surface and alumina contact areas had the greatest sulfur oxide storage capacity. As a result, we observed that the pelleted catalysts were the lowest sulfur emitters in the 75 FTP, and among the highest emitters in the HWFET. The air pump equipped monolithic catalysts operating at 4-7% tailpipe oxygen emitted the greatest sulfate and particulate matter. To decrease the rate of catalytic oxidation of SO_2 to SO_3 and hence to H_2SO_4 would be both a kinetic and thermodynamic problem and would affect catalytic oxidation of excess HC and CO, since the catalytic properties that affect HC and CO oxidation likewise affect SO_2 oxidation. Catalyst vehicle particulate matter was composed mostly of sulfate; the non-sulfate portion was composed of carbonaceous material and aluminum and iron oxidation products. No platinum was detected in the particulate matter.

Table 15. ELEMENTAL ANALYSIS OF PARTICULATE MATTER BY X-RAY FLUORESCENCE: 1975 FTP RESULTS[a]
(milligrams/mile)

Element \ Vehicle	Chevrolet Impala	Chevrolet Nova	Plymouth Fury	Plymouth Scamp	Detection limit
Si	0.052	0.022	0.012	0.013	0.001
Cd	0.001	0.002	ND	ND	0.001
Al	0.133	0.435	0.045	0.054	0.005
S	0.757	2.740	6.212	0.853	0.005
Mg	0.004	0.004	0.003	0.001	0.001
K	0.008	0.012	0.003	0.004	0.001
Zn	0.065	0.080	ND	0.019	0.010
Ni	0.008	0.008	ND	0.006	0.001
Fe	1.085	3.224	0.575	1.035	0.022
Ti	0.002	0.002	ND	ND	0.001
Ba	0.005	0.021	0.003	0.003	0.002
Ca	0.007	0.021	0.005	0.014	0.002
Pt	ND	ND	ND	ND	0.001
V	0.003	ND	ND	ND	0.001
C[b]	1.97	7.46	2.64	2.29	–
H[b]	1.13	3.37	2.35	1.56	–

[a] Vehicles run on 0.087% sulfur fuel.

[b] Combustion analysis results.

ND = Not detected.

Table 16. ELEMENTAL ANALYSIS OF PARTICULATE MATTER BY X-RAY FLUORESCENCE: HWFET RESULTS[a] (milligrams/mile)

Element \ Vehicle	Chevrolet Impala	Chevrolet Nova	Plymouth Fury	Plymouth Scamp
Si	0.026	0.020	0.017	0.013
Cd	0.001	0.003	0.001	ND
Al	0.064	0.120	0.037	0.016
S	5.721	23.885	21.694	4.686
Mg	0.003	0.005	0.005	ND
K	0.007	0.003	0.007	0.006
Zn	0.091	0.120	ND	0.026
Ni	0.005	0.011	0.008	0.026
Fe	2.309	5.456	0.316	ND
Ti	ND	ND	0.003	ND
Ba	0.005	0.004	0.004	0.007
Ca	0.008	0.008	0.087	0.015
Pt	ND	ND	ND	ND
V	ND	ND	ND	ND
C[b]	2.82	3.03	4.49	3.49
H[b]	2.27	4.72	5.04	2.79

[a] Vehicles run on 0.087% sulfur fuel.

[b] Combustion analysis results.

ND = Not detected.

Table 17.

ELEMENTAL ANALYSIS OF PARTICULATE MATTER BY X-RAY FLUORESCENCE: 1975 FTP RESULTS[a]

(milligrams/mile)

Element \ Vehicle	Ford Granada	Ford Torino	Honda CVCC
Si	0.007	0.011	0.009
Cd	ND	ND	ND
Al	0.029	0.190	0.008
S	1.397	4.729	0.125
Mg	0.002	0.002	0.005
K	0.002	0.002	0.002
Zn	0.017	0.017	0.030
Ni	ND	0.005	0.005
Fe	0.729	1.614	0.125
Ti	ND	0.002	0.001
Ba	ND	0.003	0.003
Ca	0.005	0.011	0.041
Pt	ND	ND	ND
V	ND	ND	ND
C[b]	2.39	6.41	2.13
H[b]	0.06	0.07	0.05

[a] Vehicles run on 0.041% sulfur fuel.

[b] Combustion analysis results.

ND = Not detected.

Table 18.

ELEMENTAL ANALYSIS OF PARTICULATE MATTER BY X-RAY FLUORESCENCE: HWFET RESULTS[a] (milligrams/mile)

Element \ Vehicle	Ford Granada	Ford Torino	Honda CVCC
Si	0.006	0.005	0.062
Cd	ND	0.001	ND
Al	0.008	0.047	0.060
S	5.017	10.105	2.019
Mg	0.019	0.001	0.007
K	0.002	0.002	0.011
Zn	0.016	0.015	0.035
Ni	ND	0.005	0.007
Fe	0.153	0.564	0.224
Ti	0.006	0.001	0.005
Ba	ND	0.005	0.003
Ca	0.002	0.008	0.051
Pt	ND	ND	ND
V	ND	ND	ND
C[b]	5.27	2.14	6.75
H[b]	1.10	0.20	0.26

[a] Vehicles run on 0.041% sulfur fuel.

[b] Combustion analysis results.

ND = Not detected.

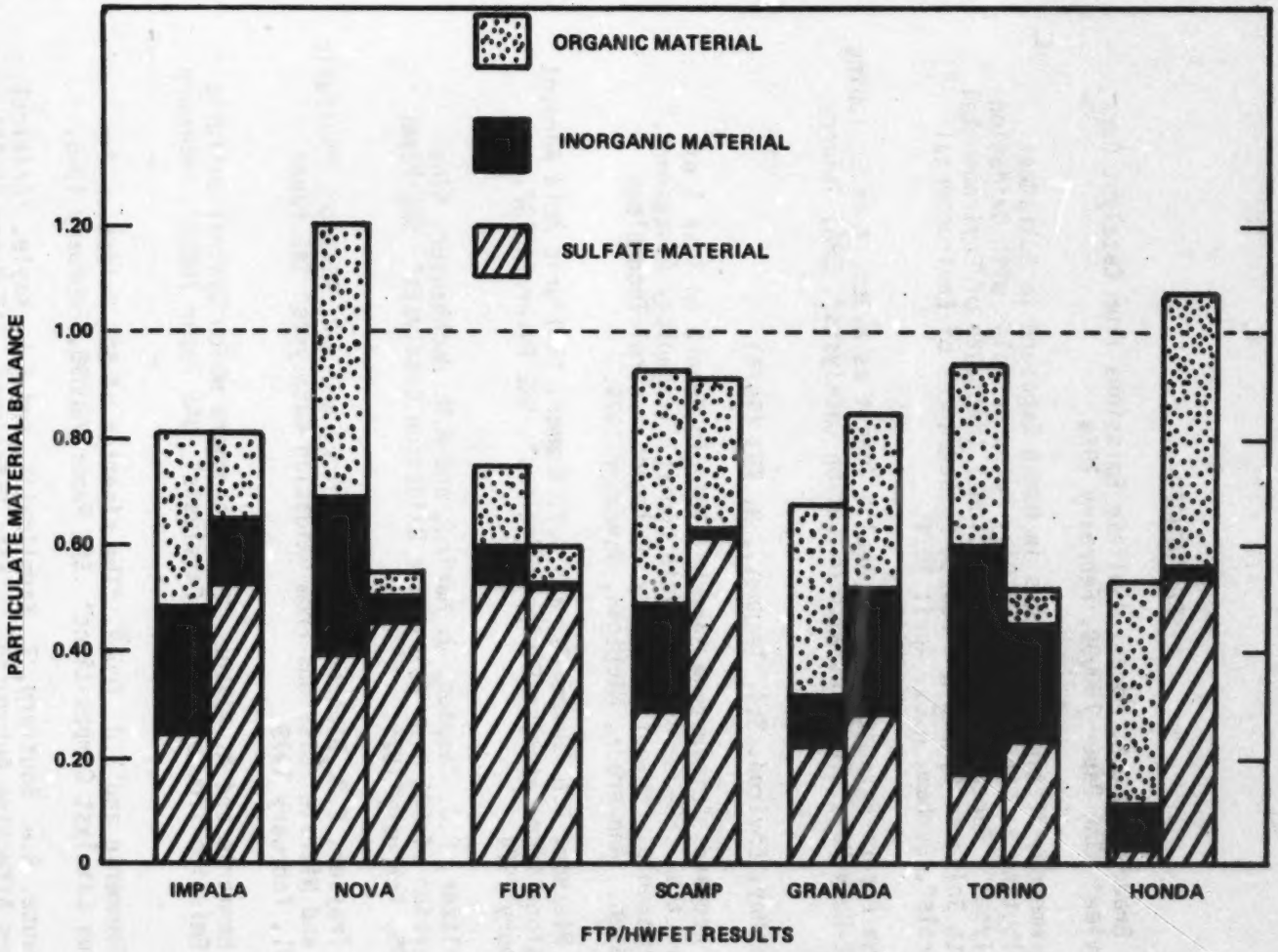

Figure 4. Vehicular particulate material balance.

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APPENDIX A
UNLEADED GASOLINE ANALYSIS

Research Octane Number	93.2
Motor Octane Number	84.7
Reid Vapor Pressure, psia	10.2
Distillation, ASTM D-86, °F	
IBP	90
10%	124
50%	203
90%	290
EP	372
Fia Analysis	
Aromatics %	24.0
Olefins %	8.3
Paraffins %	67.7
API Gravity @ 60°F	61.6
Weight % C	85.26
Weight % H	14.01
Weight % S	0.020
Lead, g/gallon	0.00004

APPENDIX B
FUEL SULFUR ANALYSIS

Amount of Thiophene in ml added to 55 gal drum of fuel	Theoretical % sulfur	Measured % sulfur
0.0	0.020	0.020[a]
37.1	0.030	0.030[b]
69.0	0.038	0.036[a]
74.1	0.040	0.041[b]
139.0	0.058	0.053[a]
148.2	0.060	0.059[b]
222.4	0.080	0.084[b]
278.7	0.095	0.087[a]

[a] Exxon Research and Engineering analysis via X-ray Method.

[b] Environmental Protection Agency analysis by ASTM Lamp Method. Estimated measurement uncertainty is $\pm$ 10%.